Polarization-dependent soft-x-ray absorption of highly oriented ZnO microrod-array

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Zinc oxide represents an important basic material (II-VI semiconductor) due to its low cost, wide bandgap as well as its electrical, optoelectronic and luminescent properties. ZnO is of importance for fundamental research as well as relevant for various fields of industrial and high technological applications. Recently, a low threshold lasing action has been observed at room temperature in highly oriented ZnO nanorod arrays. From a fundamental point of view, it is crucial to probe and understand the electronic structure of such novel materials to tailor their physical properties as well as developing novel and improved devices. A novel approach to materials chemistry has been developed which contributed to the fabrication of purpose-built nano/microparticulate thin films from aqueous solution[1]. Such well-defined and well-ordered materials should contribute to reach required enhanced fundamental knowledge of the relation between structure and physical properties.

Here we report a polarization-dependent x-ray absorption spectroscopy (XAS) study performed at synchrotron radiation facility on highly oriented ZnO microrods. The experiments were performed on BL7.0.1 at the ALS[2]. The x-ray absorption spectra were measured by recording the total electron yield while scanning the photon energy over the O *1s*-edge region at a resolution of 0.2 eV. The XAS experiments were carried out on two different (isotropic and anisotropic) homogeneous and crystalline zincite ZnO (wurtzite) thin film samples, i.e. ZnO spheres, which consist of monodisperse spherical particles of 150 nm in diameter, and ZnO microrods consisting of monodisperse, anisotropic and highly oriented crystallites grown along the c-axis and perpendicular to a transparent conducting glass substrate (F-SnO2)\cite{Vayssieres01a}. The microrods of 10 μm in length and 1.5 μm in width are oriented normal to the substrate surface.

The polarization-dependent x-ray absorption measurements are shown in Figure 1. The variations in the spectral shape continue up to 30 eV above the absorption threshold. The resolved absorption features are indicated as a_1-a_8. Prior to a_1, no polarization-dependence is observed in x-ray absorption spectra for either sample. However at higher photon energies, strong anisotropic effects are observed for the ZnO microrods (bottom spectra). Measuring at grazing incidence geometry, i.e. incidence angle θ = 10 degrees, where the absorption features a_3, a_5, and a_8 are stronger, the excitation to the state along the *c*-axis of the wurtzite structure is enhanced. At normal incidence geometry, i.e. θ = 90 degrees, where the absorption features a_2, a_4, and a_7 are stronger, the excitation to the in-plane state is enhanced. No significant change is observed for the isotropic samples of ZnO consisting of spherical particles as a function of the polarization angle. However, all the absorption features are averaged out and observed in the

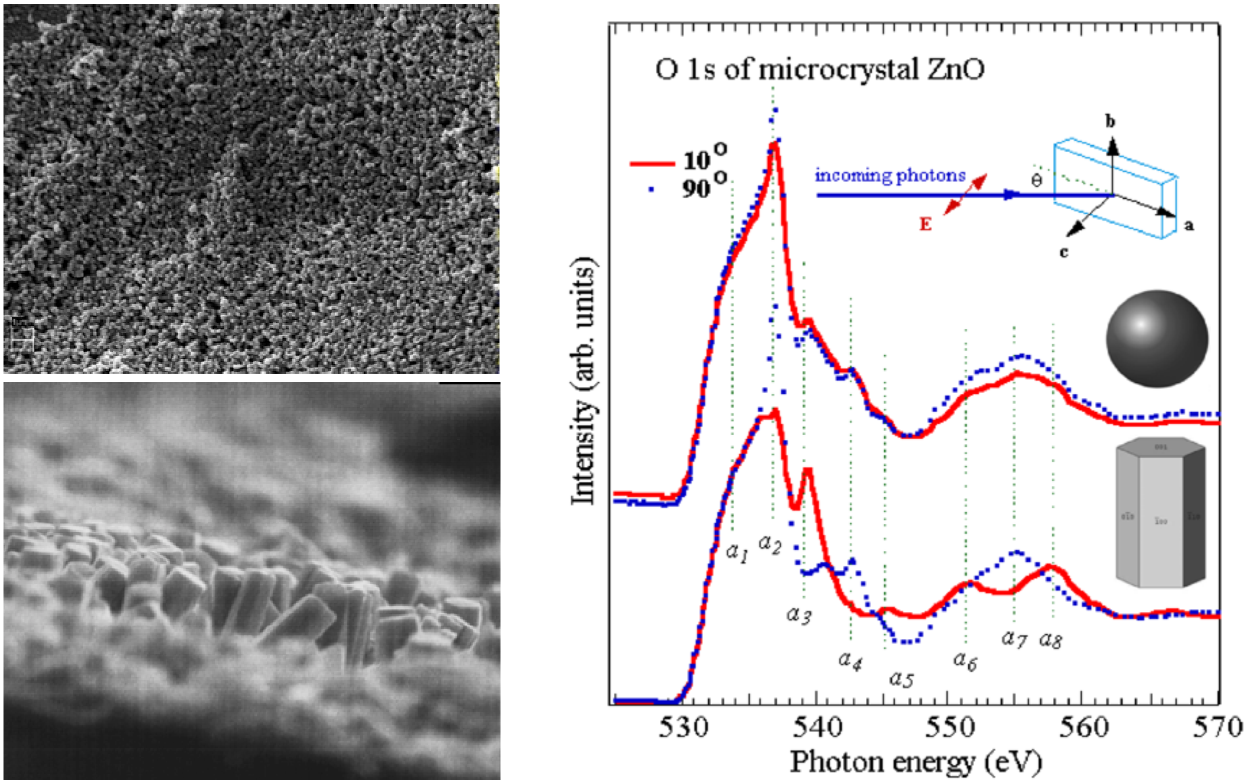

Fig. 1. Polarization-dependent x-ray absorption measurements.

XAS spectra measured with either geometrical detection. The experimental findings suggest a strong correlation between the electronic structure and the geometrical structure of the crystalline ZnO arrays. Such results demonstrate that designing materials with the appropriate morphology and orientation, i.*e purpose-built* materials, enables to reach better fundamental understanding of nano/microscale materials and their physical properties. Probing the orbital symmetry of oxygen and resolving its contribution to the conduction band of this important large band-gap II-VI semiconductor is of crucial importance for the understanding of its optoelectronic properties.

References:

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This work was supported by the Swedish Natural Science Research Council (NFR), Council for Engineering Sciences (TFR), and the Göran Gustafsson Foundation for Research in Natural Science and Medicine (GGS). Department of Energy Materials Sciences Division Contract DE-AC03-76SF00098.

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